



RECEIVED  
NOV 14 2003  
TC 1700

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of: **TAKAYANAGI, Hitoshi et al.**

Group Art Unit: 1756

Serial No.: 10/082,089

Examiner: **Dote, J.**

Filed: **February 26, 2002**

P.T.O. Confirmation No.: 8614

For. **DRY COLOR TONER FOR ELECTROSTATIC IMAGE DEVELOPMENT**

**SUBMISSION OF TRANSLATION OF CERTIFIED COPY OF  
FOREIGN PRIORITY DOCUMENT**

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Date: November 10, 2003

Sir:

Submitted herewith is a translation of the certified copy of the foreign priority document for the above-identified application. The translation is being submitted to perfect the claim for foreign priority.

Attached please find a check in the amount of \$110.00 to cover the cost of the extension for a large entity. In the event that any additional fees are due in connection with this paper, please charge our Deposit Account No. 01-2340.

Respectfully submitted,

ARMSTRONG, KRATZ, QUINTOS,  
HANSON & BROOKS, LLP

Susanne M. Hopkins  
Attorney for Applicant  
Reg. No. 33,247

SMH/mla  
Atty. Docket No. **020232**  
Suite 1000  
1725 K Street, N.W.  
Washington, D.C. 20006  
(202) 659-2930



23850

PATENT TRADEMARK OFFICE

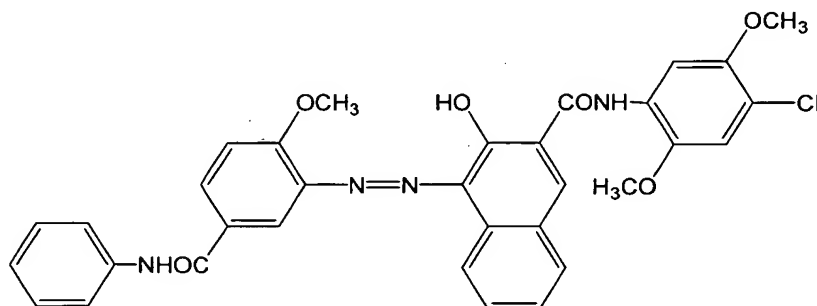
[Document Type] Specification

[Title of the Invention] Dry Color Toner for Electrostatic Image Development

[Claims]

- 5 [Claim 1] A color toner for electrostatic image development containing at least a binder resin and an organic pigment of the following formula 1, wherein an average roundness of the color toner defined in the following equation 1 is 0.97 or more.

10 Formula 1:



Equation 1:

Average roundness = (Perimeter of a circle having the same area as that of a projected area of particles) / (Perimeter of a  
15 projected image of particles)

[Claim 2] A color toner for electrostatic image development according to claim 1, wherein the binder resin is a polyester resin and/or a vinyl copolymer resin.

[Claim 3] A color toner for electrostatic image development  
20 according to claims 1 or 2, wherein the binder resin has a carboxyl group and the acid value is within a range from 1-30

KOH mg/g.

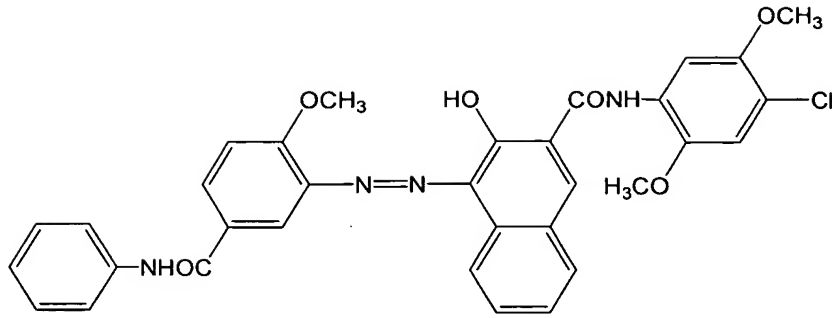
[Claim 4] A color toner for electrostatic image development according to any one of claims 1, 2 or 3, wherein a releasant is additionally contained.

5 [Claim 5] A color toner for electrostatic image development according to any one of claims 1, 2, 3 or 4, wherein the releasant contains a wax containing a higher fatty acid ester compound and/or an aliphatic alcohol compound.

[Claim 6] A color toner for electrostatic image development  
10 according to any one of claims 1, 2, 3, 4 or 5, wherein a charge control agent is additionally contained.

[Claim 7] A method of producing the color toner for electrostatic image development of claim 1, which comprises mixing a mixture containing a binder resin having a carboxyl  
15 group and an organic pigment represented by the following formula 1 with an aqueous medium in the presence of a base to prepare a colored particle suspension in which the colored particles comprising the mixture are emulsified in the aqueous medium, separating the colored particles from the colored  
20 particle suspension, and drying the colored particles.

Formula 1:



[Claim 8] A method of producing the color toner for electrostatic image development according to claim 7, wherein the mixture is prepared by previously dissolving or dispersing a binder resin having a carboxyl group in the mixture and a colorant in an organic solvent and wherein the colored particle suspension is produced by adding a phase inversion accelerator in the process of producing the colored particle suspension.

[Claim 9] A method of producing the color toner for electrostatic image development according to claim 8, wherein the phase inversion accelerator is an alcohol solvent.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a toner for electrostatic image development, which is preferably employed in electrophotographic copying machines, printers, and facsimiles, and is also employed in toner-jet printers.

[0002]

[Prior Art]

Toner compositions produced by dispersing a black colorant such as carbon black in a binder resin are often used to obtain a visible image by means of the electrophotographic method. However, full-color or monochrome copying machines and printers have recently been developed which employ color toners produced by dispersing a chromatic color pigment such as cyan pigment, magenta pigment, or yellow pigment in a binder.

[0003]

Properties required of these color toners include color reproducibility, for example, the image after printing has a clear color developability, the color toner exhibits an excellent transparency in color overlapping during multi-color printing and has a clear color reproducibility without causing color turbidity, or the color toner achieves a clear color free from turbidity when projected a color image obtained by transferring and fixing on an overhead projector (hereinafter referred to as an OHP) sheet on a screen.

[0004]

Furthermore, cost reduction and size reduction of machines as well as power saving and resource conservation have recently been studied. With the spread of color printers and color copying machines, high definition and a broad gradational range have been required in printing properties of machines. Thus, properties, which enable one to conduct

printing having the same definition and gradation as those in the case of offset printing, have been required of toners.

[0005]

To improve the definition and gradation of the printed image, the particle size of the toner must be reduced compared with a conventionally used toner having an average particle size within a range from 7-15  $\mu\text{m}$ . Since the content of a colorant in a conventional toner is within a range from about 2-5%, a comparatively large amount of the toner must be transferred and fixed onto a material to be printed so as to obtain a desired printing density. As a result, the toner has such drawbacks that the resulting printed image has a large thickness as compared with a print, which is obtained by using an offset printing ink containing a pigment in the amount which is several to several tens of times as much as that of the toner, resulting in different volume. This tendency is particularly conspicuous in the case of reproducing neutral tints by printing with overlaying plural color toners. For example, in the case of printing on a matte coated paper or wood free paper, the resulting printed image has a volume, that is different from that of a paper, and also has a gloss, thus making it difficult to conduct subdued printing.

[0006]

Therefore, color toners have recently been desired which contain a large amount of colorant, which have a small

particle size, and which do not remain on an intermediate transferring material after being developed on a photosensitive material so as to be transferred onto a material to be printed, such as paper, at a high transfer efficiency. Such a color toner can reproduce the same image quality and volume as those in the case of offset printing and can also reduce the amount of the toner required for printing, thus making it possible to reduce the printing cost.

[0007]

10        Among powdered toners produced by a conventionally employed pulverization method, in principle, a small particle size is possible. However, a toner having a small particle size produced by the pulverization method is not actually suited for practical use because it has drawbacks that (1) it  
15 becomes difficult to control the charge because of an increase in the ratio of releasants such as colorants and waxes exposed on the surface of the toner particles, (2) the fluidity of the powder is lowered by the nonuniform shape of the toner particles and (3) the energy cost required for the production  
20 increases.

[0008]

Under these circumstances, development of a spherical toner having a small particle size has intensified using the polymerization method. Although various methods have been  
25 known as the method of producing a toner using the

polymerization method, the suspension polymerization method has widely been employed, which comprises uniformly dissolving and dispersing a monomer, a polymerization initiator, a colorant and a charge control agent, adding the mixture in an aqueous medium in the presence of a dispersion stabilizer while stirring to form oil droplets and polymerizing the monomer to obtain toner particles. Although the reduction in particle diameter and spheroidizing can be satisfactorily conducted by the suspension polymerization method, a principal component of the binder resin is limited to a radically-polymerizable vinyl polymer and toner particles made of a polyester resin or epoxy resin suited for use as a color toner cannot be produced by the suspension polymerization method. It is difficult to reduce VOC (volatile organic compound made of an unreacted monomer) by the suspension polymerization method.

[0009]

[Problems to be Solved by the Invention]

Under these circumstances described above, the present invention has been achieved and an object thereof is to provide a color toner for electrostatic image development, which gives a clear image after printing and has an excellent color reproducibility in color overlapping during multi-color printing, and also which gives an image having a transparency fixed on an OHP sheet and can achieve a clear color free from



turbidity when projected on a screen. Another object of the present invention is to provide a color toner for electrostatic image development having a small particle size, which has a large content of a colorant as compared with a conventional color toner. Still another object of the present invention is to provide a color toner for electrostatic image development, which does not remain on an intermediate transferring material after being developed on a photosensitive material so as to be transferred onto a material to be printed, such as paper, at a high transfer efficiency. A further object of the present invention is to provide a method of producing a color toner for electrostatic image development, which achieves the objects described above.

[0010]

15 [Means for Solving the Problem]

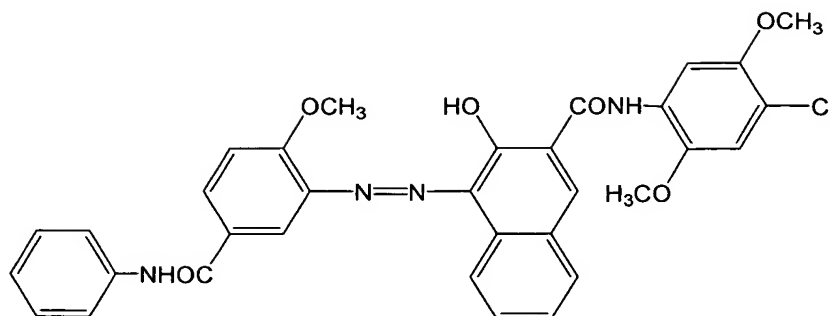
As a result of diligent research, the present inventors have found that the objects described above can be achieved by employing a spherical color toner that uses a magenta pigment having a specific structure, thus completing the present invention.

20 [0011]

That is, the present invention provides a color toner for electrostatic image development containing at least a binder resin and an organic pigment of the following formula 1, wherein an average roundness of the color toner defined in the

following equation 1 is 0.97 or more.

Formula 1:



Equation 1:

$$\text{Average roundness} = \frac{\text{Perimeter of a circle having the same area as that of a projected area of particles}}{\text{Perimeter of a projected image of particles}}$$

5

[0012]

The present invention also provides a method of producing color toner for electrostatic image development, which comprises mixing a mixture containing a binder resin having a carboxyl group and an organic pigment represented by the  
10      aforementioned formula 1 with an aqueous medium in the presence of a base to prepare a colored particle suspension in which the colored particles comprising the mixture are emulsified in the aqueous medium, separating the colored  
15      particles from the colored particle suspension, and drying the colored particles to produce the above color toner in which the average roundness is 0.97 or more.

[0013]

[Embodiments of the Invention]

20

The present invention will now be described in detail.

The color toner for electrostatic image development of the present invention contains at least a binder resin and an organic pigment of the aforementioned formula 1, and the binder resin employed in the present invention is not

specifically limited as long as it does not interfere with the objects of the present invention. Specific examples thereof include vinyl copolymer resin such as polystyrene resin, styrene-acrylic resin, or styrene-butadiene resin, and polyester resin, epoxy resin, butyral resin, xylene resin, and coumarone-indene resin. Among these binder resins, vinyl copolymer resin and polyester resin are preferred, and polyester resin can be employed particularly preferably because of its good balance between the fixing properties, anti-offset properties and transparency.

[0014]

The polyester resin is synthesized by dehydration condensation of a polybasic acid and a polyhydric alcohol. Examples of the polybasic acid include aromatic carboxylic acids such as terephthalic acid, isophthalic acid, phthalic anhydride, trimellitic anhydride, pyromellitic acid, and naphthalenedicarboxylic acid; aliphatic carboxylic acids such as maleic anhydride, fumaric acid, succinic acid, alkenylsuccinic anhydride, and adipic acid; and alicyclic carboxylic acids such as cyclohexanedicarboxylic acid. These polybasic acids can be used alone or in combination. Among

these polybasic acids, an aromatic carboxylic acid is preferably employed.

[0015]

Examples of the polyhydric alcohol include aliphatic diols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, butanediol, hexanediol, neopentyl glycol, glycerin, trimethylolpropane, and pentarythritol; alicyclic diols such as cyclohexanediol, 1,4-cyclohexanedimethanol, and hydrogenated bisphenol A; and aromatic diols such as ethylene oxide adduct of bisphenol A and propylene oxide adduct of bisphenol A. These polyhydric alcohols can be used alone or in combination. Among these polyhydric alcohols, aromatic diols and alicyclic diols are preferred and aromatic diols are more preferred.

15 [0016]

A hydroxyl group at polymer terminal and/or a carboxyl group may be esterified by further adding monocarboxylic acid and/or monoalcohol to the polyester resin obtained by the polycondensation of the polyhydric carboxylic acid and polyhydric alcohol, thereby controlling the acid value of the polyester resin.

[0017]

Examples of the monocarboxylic acid employed for the purpose include acetic acid, acetic anhydride, benzoic acid, trichloroacetic acid, trifluoroacetic acid, and propionic

25

anhydride. Examples of the monoalcohol include methanol, ethanol, propanol, octanol, 2-ethylhexanol, trifluoroethanol, trichloroethanol, hexafluoroisopropanol, and phenol.

[0018]

5           The polyester resin can be produced by the condensation reaction of the polyhydric alcohol and polyhydric carboxylic acid according to a conventional method. For example, it can be produced by charging the polyhydric alcohol and polyhydric carboxylic acid in a reaction vessel equipped with a  
10 thermometer, a stirrer and a dropping condenser, heating them to 150-250°C in the presence of an inert gas such as nitrogen gas, continuously removing a low-molecular compound out of the reaction system, terminating the reaction at a point in time when the acid value reached a predetermined value, and cooling  
15 to obtain a desired reaction product.

[0019]

          In the synthesis of the polyester resin, a catalyst may be employed. Examples of the catalyst include esterification catalysts, for example, organometallic compound (e.g.  
20 dibutyltin dilaurate and dibutyltin oxide, etc.) and metal alkoxide (e.g. tetrabutyl titanate, etc.). In the case in which the carboxylic acid component is a lower alkyl ester, ester interexchange catalysts can be used, for example, metal acetate (e.g. zinc acetate, lead acetate, magnesium acetate,  
25 etc.), metal oxide (e.g. zinc oxide, antimony oxide, etc.) and

metal alkoxide (e.g. tetrabutyl titanate, etc.). The amount of the catalyst is preferably within a range of 0.01-1% by weight based on the total amount of the raw materials.

[0020]

5 In the polycondensation reaction, a polybasic acid having three or more carboxyl groups in a molecule or an anhydride thereof and/or a polyhydric alcohol having three or more hydroxyl groups in a molecule may be used particularly to prepare a crosslinked polyester resin.

10 [0021]

The vinyl copolymer which can be employed in the present invention is preferably a copolymer resin of a styrene (meth)acrylate ester. Examples of the styrene monomer include styrene,  $\alpha$ -methylstyrene, vinyltoluene, p-sulfonestyrene and

15 dimethylaminoethylstyrene.

[0022]

Examples of the (meth)acrylate ester monomer include alkyl (meth)acrylate such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tertiary butyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, or stearyl (meth)acrylate; alicyclic (meth)acrylate such as cyclohexyl (meth)acrylate; aromatic

25 (meth)acrylate such as benzyl (meth)acrylate; hydroxyl group-

containing (meth)acrylate such as hydroxyethyl  
(meth)acrylate; phosphoric acid group-containing  
(meth)acrylate such as (meth)acryloxyethyl phosphate; halogen  
atom-containing (meth)acrylate such as 2-chloroethyl  
5 (meth)acrylate, 2-hydroxy-3-chloropropyl (meth)acrylate, or  
2,3-dibromopropyl (meth)acrylate; epoxy group-containing  
(meth)acrylate such as glycidyl (meth)acrylate; ether group-  
containing (meth)acrylate such as 2-methoxyethyl  
(meth)acrylate or 2-ethoxyethyl (meth)acrylate; and basic  
10 nitrogen atom- or amide group-containing (meth)acrylate such  
as dimethylaminoethyl (meth)acrylate or diethylaminoethyl  
(meth)acrylate.

[0023]

A copolymerizable unsaturated compound can also be used,  
15 if necessary. For example, a carboxyl group-containing vinyl  
monomer can be used such as (meth)acrylic acid, itaconic acid,  
crotonic acid, maleic acid, or fumaric acid; sulfo group-  
containing vinyl monomer such as sulfoethylacrylamide; nitrile  
group-containing vinyl monomer such as (meth)acrylonitrile;  
20 ketone group-containing vinyl monomer such as vinyl methyl  
ketone or vinyl isopropenyl ketone; and basic nitrogen atom-  
or amide group-containing vinyl monomer such as N-  
vinylimidazole, 1-vinylpyrrole, 2-vinylquinoline, 4-  
vinylpyridine, N-vinyl-2-pyrrolidone, or N-vinylpiperidone.

25 [0024]

A crosslinking agent can be used in an amount within a range of 0.1-2% by weight based on the vinyl monomer.

Examples of the crosslinking agent include divinylbenzene, divinyl naphthalene, divinyl ether, ethylene glycol

5 di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, 1,6-hexane glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, propylene glycol di(meth)acrylate, 10 dipropylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, and tetramethylolmethane tetra(meth)acrylate.

[0025]

As the method of producing the copolymer of styrene (meth)acrylate ester, a conventional polymerization method can 15 be used. Examples thereof include methods of conducting the polymerization reaction in the presence of a polymerization catalyst, for example, solution polymerization, suspension polymerization, and bulk polymerization.

20 [0026]

Examples of the polymerization catalyst include 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobisisobutyronitrile, 1,1'-azobis(cyclohexane-1-carbonitrile), benzoyl peroxide, dibutyl peroxide, and 25 butylperoxy benzoate, and the amount is preferably within a



range of about 0.1-10.0% by weight based on the vinyl monomer component.

[0027]

The glass transition temperature ( $T_g$ ) of the binder resin employed in the present invention is preferably 50°C or higher, and particularly preferably 55°C or higher. When the glass transition temperature  $T_g$  is lower than 50°C, the resulting toner tends to cause blocking (thermal agglomeration) during the storage or conveying, or exposure to high temperature in a developing apparatus.

[0028]

The softening point of the binder resin employed in the present invention is 90°C or higher, preferably within a range of 90-180°C, and more preferably within a range of 95-160°C. When the softening point is lower than 90°C, the toner is liable to cause agglomeration phenomenon, resulting in problems during the storage and printing. On the other hand, when the softening point exceeds 180°C, the fixation properties are often lowered.

[0029]

In the case in which the color reproducibility during the color overlapping and the transparency during the fixation on the OHP sheet are required in the full-color toner, the softening point of the resin is preferably within a range of 90-130°C, and more preferably in a range of 95-120°C.

[0030]

The softening point of the resin in the present invention is defined by a T1/2 temperature as measured by employing a Flow Tester "CFT-500" manufactured by Shimadzu Corporation as a constant load extrusion type capillary rheometer. Employing a flow tester, the measurement was conducted under the conditions of a piston cross section of 1 cm<sup>2</sup>, a cylinder pressure of 0.98 MPa, a die length of 1 mm, a nozzle diameter of 1 mm, a measurement initiation temperature of 50°C, a heating rate of 6°C/min. and a sample weight of 1.5 g.

[0031]

The acid value of the binder resin used in the present invention is preferably not more than 1-30 mgKOH/g. The acid value is preferably within the above range in the production of the spherical toner. The environmental stability is improved when used as the toner.

[0032]

The shape of a toner particle in the toner for electrostatic image development of the present invention is spherical or generally spherical having an average roundness, defined by the following equation,

Average roundness =  $\frac{\text{Perimeter of a circle having the same area as that of a projected area of particles}}{\text{Perimeter of a projected image of particles}}$   
of preferably 0.97 or more, and particularly preferably 0.98 or more.

[0033]

The color toner for electrostatic image development of the present invention can secure a good powder fluidity even if size reduction is conducted by achieving such spherical or generally spherical particles. Also a good transfer efficiency can be secured, thus obtaining an excellent image quality (definition, gradation). When the average roundness is less than 0.97, that is, the shape is more like an irregular shape from the spherical shape, the transfer efficiency is lowered and, therefore, it is not preferred.

10 The average roundness is also determined by taking a SEM (scanning electron microscope) photograph of the toner particles, followed by measurement and calculation. In the present invention, the average roundness is measured by employing a flow type particle image analyzer FPIP-1000

15 manufactured by Toa Iyo Denshi Co., Ltd.

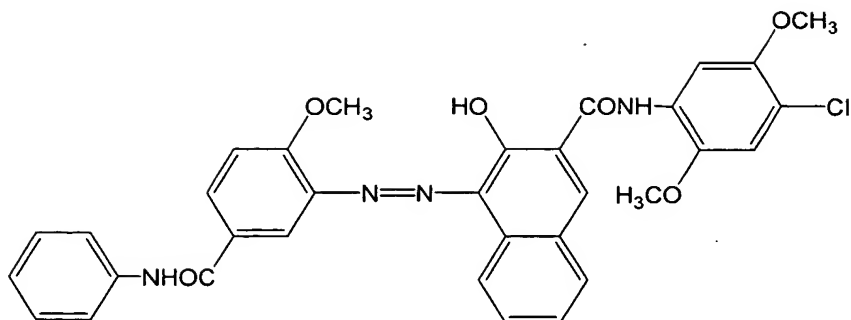
[0034]

In the present invention, organic pigment C.I. Pigment Red 146 represented by formula 1 is used. The use of this pigment makes it possible to obtain a color toner having good transfer properties as compared with a magenta pigment that has conventionally been employed in the toner, for example, C.I. Pigment Red 57:1 or C.I. Pigment Red 122. It is also possible to print a high-quality image, which shows stable charge behavior during continuous printing and is superior in

25 color reproducibility and transparency.

Formula 1:

[0035]



[0036]

5        The amount of the organic pigment of the formula 1 used in the present invention is preferably from 1-50 parts by weight, more preferably from 2-30 parts by weight, and particularly preferably from 2-20 parts by weight, based on 100 parts by weight of the binder resin.

10    [0037]

      In the present invention, in addition to the organic pigment of the formula 1, other colorants can be used to control the color hue. These colorants include conventionally known colorants. Examples of blue colorants include

15    phthalocyanine C.I. Pigment Blue 15-3 and indanthrone C.I. Pigment Blue 60; examples of red colorants include quinacridone C.I. Pigment Red 122, azo C.I. Pigment Red 22, C.I. Pigment Red 48:1, C.I. Pigment Red 48:3 and C.I. Pigment Red 57:1; examples of the yellow colorants include azo C.I.

20    Pigment Yellow 12, C.I. Pigment Yellow 13, C.I. Pigment Yellow 14, C.I. Pigment Yellow 17, C.I. Pigment Yellow 97, C.I.

Pigment Yellow 155, benzimidazolone C.I. Pigment Yellow 151, C.I. Pigment Yellow 154 and C.I. Pigment Yellow 180.

[0038]

As long as the objects of the present invention are not  
5 impaired, the pigments described above can be used in  
combination with the magenta pigment of the formula 1. For  
example, an orange toner can be produced by using in  
combination with the yellow pigment and a bluish purple toner  
can be produced by using in combination with the cyan pigment.  
10 When using the pigment of the formula 1 in combination with  
the other pigment, the amount of the pigment of the formula 1  
is preferably 40% by weight or more, more preferably 50% by  
weight or more, and particularly preferably 60% by weight or  
more.

15 [0039]

In the toner, various conventionally known waxes, for  
example, polypropylene wax, polyethylene wax, polyamide wax  
and Fischer-Tropsch wax can be appropriately used as a  
releasant. It is preferable to use a wax containing a higher  
20 fatty acid ester compound and/or an aliphatic alcohol  
compound, among these waxes.

[0040]

Among waxes containing a higher fatty acid ester compound  
and/or an aliphatic alcohol compound, natural waxes such as  
25 carnauba wax, montan ester wax, rice wax and wax from scale

insects; and/or synthetic ester waxes are particularly preferred. As the synthetic ester wax, a tetrabeheenate ester of pentarythritol is particularly preferable.

[0041]

5           These waxes exhibit good dispersibility especially to the polyester resin and markedly improve the fixing properties and anti-offset properties. When using these waxes as a toner for non-magnetic one-component development in the case of printing a number of sheets over a long time, they stably charge the  
10   toner without being deposited on a charge material pressed against a developing sleeve, thus making it possible to print a high-grade and fine image free from image defects and contamination. When a color toner is produced by using in combination with the colorant of the formula 1 of the present  
15   invention, it is made possible to obtain a color toner having excellent transparency as compared with a hydrocarbon wax such as polypropylene wax. The color toner having these properties has transparency and is suited for use in printing on an OHP sheet that requires a sharp projected image, and printing of a  
20   neutral color having good color reproducibility by overlapping of two or more colors.

[0042]

          A carnauba wax containing no free fatty acid obtained by purifying to remove free fatty acid is preferably used. An  
25   acid value of the carnauba wax free from free fatty acid is

preferably 3 or less, and more preferably 2 or less. The carnauba wax free from free fatty acid is in the form of a fine crystal as compared with a conventional carnauba wax, and therefore, the dispersibility in the polyester resin is improved. The montan wax is purified from a mineral and is formed into a fine crystal by purification, like carnauba wax, and thus the dispersibility in the polyester resin is improved. The acid value of the montan wax is particularly preferably 30 or less. Rice wax is obtained by purifying rice bran wax and the acid value is preferably 13 or less. The wax from scale insects can be obtained by melting a wax component secreted by larva of scale insects (*Ericerus pela*) in hot water, separating the upper layer and solidifying the upper layer with cooling, or repeating this operation. The wax from scale insects purified by such a means is white in a solid state and exhibits a very sharp melting point and is therefore suited for use as a wax for toner in the present invention. As a result of purification, the acid value becomes 10 or less, and the acid value of 5 or less is suited for use as the toner.

[0043]

These waxes may be employed alone or in combination and good anti-offset properties can be obtained by mixing with the binder resin in the amount within a range of 0.3-40 parts by weight, and preferably within a range of 1-30 parts by weight.

The amount is more preferably within a range of 1-20 parts by weight. When the amount is smaller than 0.3 parts by weight, the anti-offset properties are impaired. On the other hand, when the amount is larger than 40 parts by weight, the

5 fluidity of the toner becomes inferior and, furthermore, spent carrier occurs as a result of deposition on the surface of the carrier, thereby exerting an adverse influence on charge properties of the toner in the two-development system, and to deposit on a layer control member pressure-welded on a  
10 developing roll.

[0044]

In the present invention, charge control agents can be used, if necessary. Examples of the positive charge control agent include resins containing nigrosine dyes, quaternary  
15 ammonium salts, and resins containing quaternary ammonium salts and/or resins having amino groups. Examples of the negative charge control agent include resins containing trimethylethane dye, metal complex salt of salicylic acid, metal complex salt of benzilic acid, copper phthalocyanine,  
20 perylene, quinacridone, azo pigment, metal complex salt azo dye, heavy metal-containing acidic dye such as azochrome complex, calixarene type phenol condensate, cyclic polysaccharide, and resins containing carboxyl groups and/or sulfonyl groups.

25 [0045]



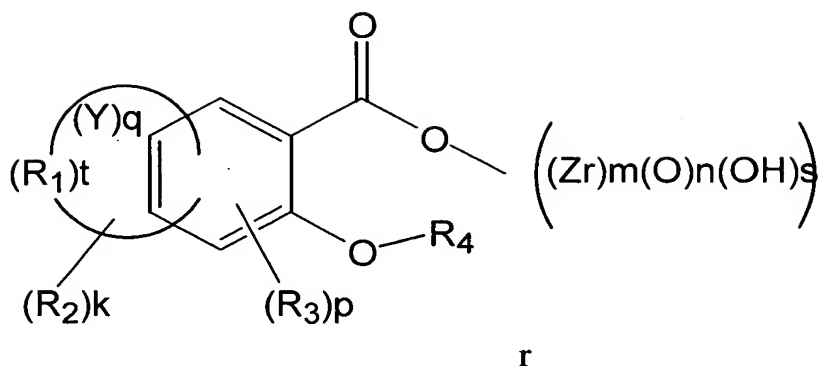
In the present invention, a colorless charge control agent is preferably used. As the negative charge control agent, BONTORON E-84 (manufactured by Orient Chemical) as a metal complex compound of salicylic acid can be preferably used. As the colorless positive charge control agent, those having a quaternary ammonium salt structure, for example, TP-302, TP-415 and TP-610 (manufactured by Hodogaya Chemical Industries Co., Ltd.), BONTORON P-51 (manufactured by Orient Chemical), and Copy Charge PSY (manufactured by Clariant Japan) are preferably used. Examples of the positive charge control agent having quaternary ammonium groups and/or amino groups include "FCA-201-PS" (manufactured by Fujikura Chemicals Co., Ltd.).

[0046]

Among these charge control agents, a compound of the following general formula 1 and a compound of the following general formula 2 can be used particularly preferably as the charge control agent in the present invention.

General formula 1

[0047]



(wherein  $R_1$  represents quaternary carbon, methine or methylene and may have a hetero atom such as N, S, O or P; Y represents a cyclic structure bonded through a saturated bond or an

5 unsaturated bond;  $R_2$  and  $R_3$  each independently represents an alkyl group, an alkenyl group, an alkoxy group, an aryl, aryloxy, aralkyl or aralkyloxy group which may have a substituent, a halogen group, hydrogen, a hydroxyl group, an amino group which may have a substituent, a carboxyl group, a

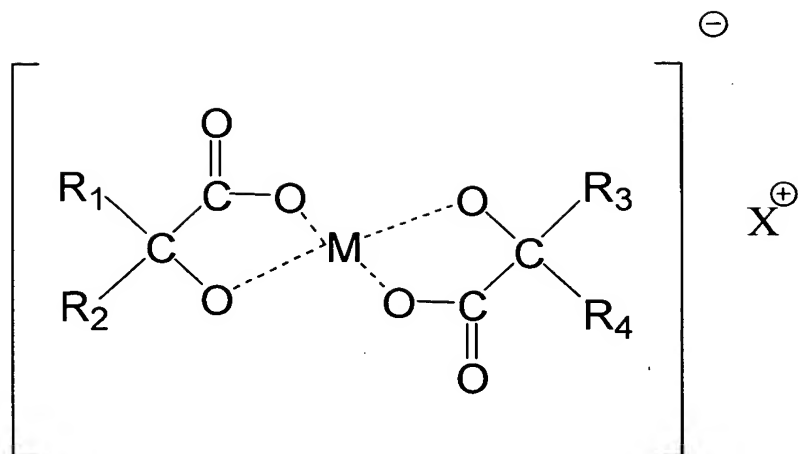
10 carbonyl group, a nitro group, a nitroso group, a sulfonyl group, or a cyano group;  $R_4$  represents hydrogen or an alkyl; t represents 0 or an integer of 1-12; m represents an integer of 1-20; n represents 0 or an integer of 1-20; k represents 0 or an integer of 1-4; p represents 0 or an integer of 1-4; q

15 represents 0 or an integer of 1-3; r represents 1-20; and s represents 0 or an integer of 1-20.)

[0048]

General formula 2:

[0049]



(wherein  $R_1$  and  $R_4$  represent a hydrogen atom, an alkyl group, or a substituted- or non-substituted aromatic ring (also containing a condensed ring);  $R_2$  and  $R_3$  a substituted- or non-

5 substituted aromatic ring (also containing a condensed ring);  $M$  represents a trivalent metal selected from B, Al, Fe, Ti, Co and Cr; and  $X^+$  represents a cation

[0050]

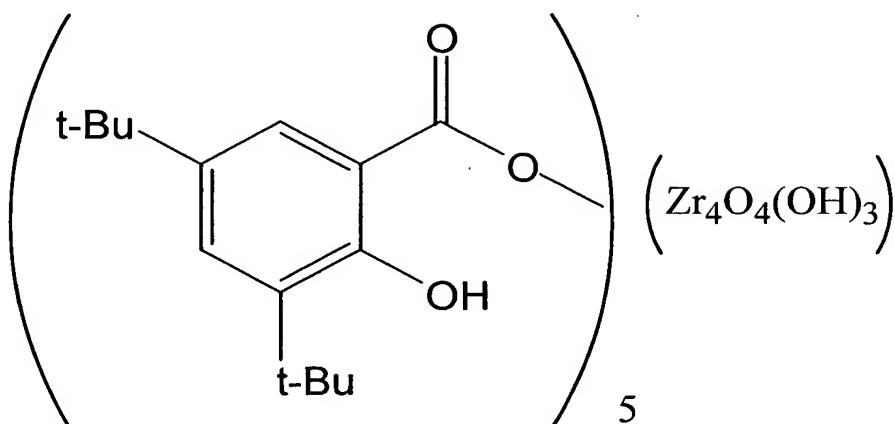
Specific examples of the compound of the general formula

10 1 include the following charge control agent 1 to charge control agent 3.

[0051]

Charge control agent 1:

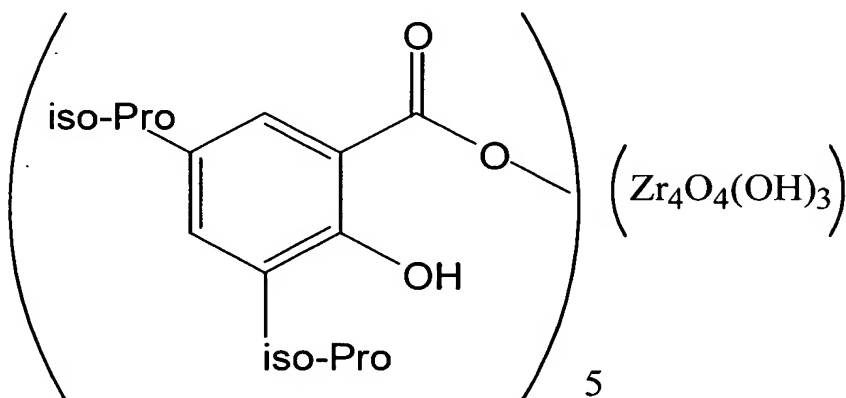
[0052]



[0053]

5 Charge control agent 2:

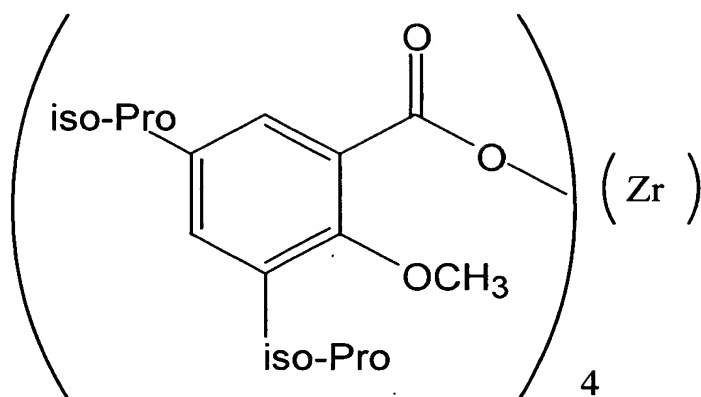
[0054]



[0055]

Charge control agent 3:

[0056]



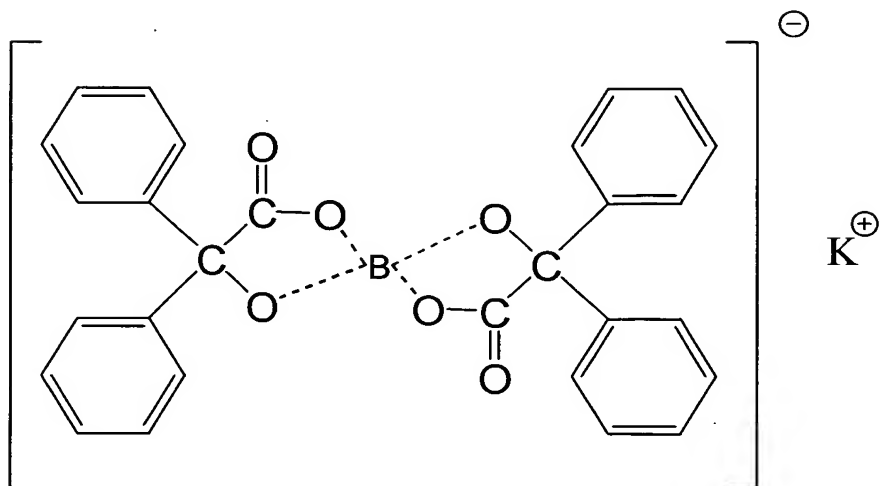
[0057]

5 Specific examples of the compound of the general formula 2 include the following charge control agent 4 and charge control agent 5.

[0058]

Charge control agent 4:

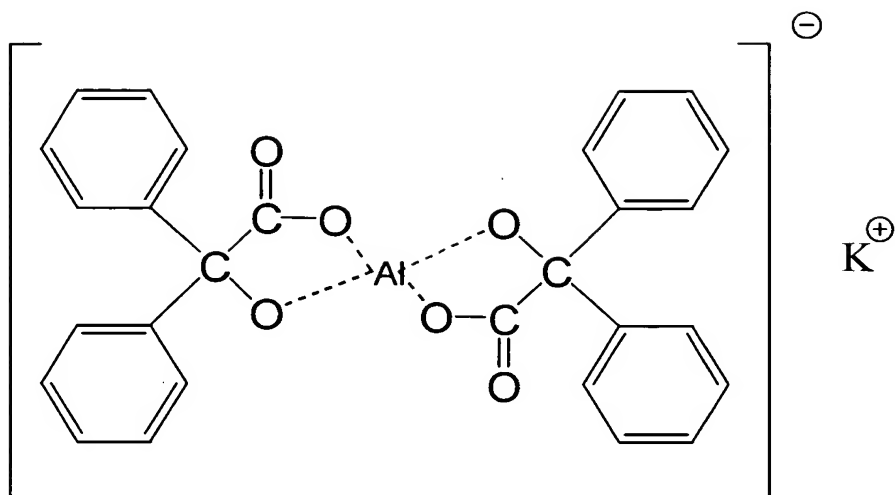
10 [0059]



[0060]

Charge control agent 5:

[0061]



[0062]

5        These charge control agents may be used alone or in combination and good charge properties can be obtained by mixing with the binder resin in the amount within a range of 0.3-15 parts by weight, and preferably from 0.5-5 parts by weight.

10    [0063]

      The color toner for electrostatic image development of the present invention is produced by mixing a mixture containing a binder resin having a carboxyl group and an organic pigment of the formula 1 with an aqueous medium in the presence of a base to prepare a colored particle suspension in which the colored particles comprising the mixture are emulsified in the aqueous medium, separating the colored particles from the colored particle suspension, and drying the

15

colored particles. In this case, the toner of the present invention can also be produced by mixing a releasant with the binder resin and the organic pigment of the formula 1, if necessary.

5 [0064]

To retain good friction charge properties even when the particle diameter of the toner is reduced, it is effective to prevent the colorant from being exposed on the surface of the toner particles, that is, to attain a toner structure wherein  
10 the colorant is contained in the toner particles. The impairment of the charge properties accompanying the reduction in particle diameter of the toner is also caused by the fact that the colorant and other additives (e.g. releasants, etc.) are partially exposed on the surface of the toner particles.  
15 Even if the content (% by weight) of the colorant is the same, the surface area of the toner particles is increased by the reduction in particle diameter and the proportion of the colorant and releasant or the like to be exposed on the surface of the toner particles is increased. As a result, the  
20 composition of the surface of the toner particles drastically changes and the friction charge properties of the toner particles drastically change, thereby making it difficult to obtain proper charge properties.

[0065]

25 According to the color toner for electrostatic image

development produced by the method of the present invention, since the colorant and the releasant, which is optionally added, are included in the binder resin, it is made possible to achieve the object of the present invention, thus obtaining  
5 a good printed image.

[0066]

It can be easily judged, for example, by observing the cross section of the particles employing TEM (transmission electron microscope) to examine that the colorant and  
10 releasant or the like are not exposed on the surface of the toner particles. More concretely, when the cross section, which was obtained by embedding the toner particles into a resin and cutting the resulting sample by a microtome, is optionally dyed with ruthenium tetroxide and observed by TEM,  
15 it can be confirmed that the pigment and releasant were included and dispersed in particles almost uniformly.

[0067]

The mixture containing a binder resin having a carboxyl group, a colorant and a releasant, which is optionally added,  
20 can be prepared by a conventionally known method. For example, the mixture is prepared by the method of mixing these raw powders and sufficiently kneading employing any of a twin-screw extruder, a kneader and a twin roll. Since the breakage of the high-molecular component of the binder resin occurs  
25 sometimes in such a melt-kneading step, it is preferable to



select the raw resin after previously confirming a change in molecular weight during the kneading of the binder resin.

[0068]

As the method of mixing the kneaded mixture thus prepared  
5 with the aqueous medium and emulsifying the admixture, for example, a method of emulsifying the kneaded mixture in the aqueous medium by applying high-speed stirring conditions in the presence of a base can be employed. Particularly, when employing this process, it is preferably prepared under the  
10 conditions of high temperature and high pressure where the binder resin is softened, thereby making it possible to inhibit the aqueous medium from boiling.

[0069]

The color toner for electrostatic image development of  
15 the present invention can also be produced by the method of mixing a binder resin and a colorant with an organic solvent, and kneading and dispersing the mixture employing the wet process to obtain the above mixture. In this case, the colorant and releasant as the other additive may be kneaded  
20 and dispersed, separately, employing the wet process.

[0070]

Concretely, it is a method of dissolving the binder resin in the organic solvent, adding the colorant and the like, dispersing them employing a general mixing/dispersing  
25 apparatus such as despa (dispersion stirrer), ball mill, bead

mill, sand mill, continuous bead mill or the like, to prepare a resin solution wherein the colorant and releasant are finely dispersed in the organic solvent, mixing the resin solution with an aqueous medium in the presence of a basic neutralizer, 5 thereby emulsifying them, and removing the organic solvent under reduced pressure to prepare the suspension of the colored particles. Then, the colored particles are separated from the suspension of the colored particles and dried to obtain a toner. This method is better than the above method 10 of producing toner via the aforementioned melt-kneading step wherein high shear is applied to the resin, because the molecular chain of the high-molecular component is not broken, even when the high-molecular component (gel component) exists in the binder resin.

15 [0071]

The binder resin employed to produce the color toner for electrostatic image development of the present invention is a resin having a carboxyl group. The binder resin having a carboxyl group is converted into a resin with the self-water 20 dispersion by neutralizing the carboxyl group as an acidic group. With respect to the resin with the self-water dispersion, the hydrophilicity increases by converting the carboxyl group into an anion, whereby the resin is dispersed in the aqueous medium (water or a liquid medium containing 25 water as a principal component).

[0072]

Examples of the base employed to neutralize the acidic group (carboxyl group) include, but are not limited to, inorganic bases such as sodium hydroxide, potassium hydroxide, and ammonia; and organic bases such as diethylamine, triethylamine, and isopropylamine.

[0073]

Examples of the organic solvent employed to dissolve or disperse the binder resin, colorant and releasent, which is optionally added, include hydrocarbons such as pentane, hexane, heptane, benzene, toluene, xylene, cyclohexane, and petroleum ether; halogenated hydrocarbons such as methylene chloride, chloroform, dichloroethane, dichloroethylene, trichloroethane, trichloroethylene, and carbon tetrachloride; ketones such as acetone, methyl ethyl ketone, and methyl isobutyl ketone; and esters such as ethyl acetate and butyl acetate. These solvents can be employed alone, or two or more kinds thereof can be employed in combination. The organic solvent dissolves the binder resin and is preferably a solvent having relatively low toxicity and low boiling point, which is easily removed in the subsequent processes. Among these organic solvents, methyl ethyl ketone is most preferable.

[0074]

A phase inversion accelerator is preferably added while a mixture made of a binder resin, a colorant, and an organic

solvent is mixed with an aqueous medium and emulsified in the presence of a base. As used herein, the term "phase inversion accelerator" refers to those having a phase inversion acceleration function. In the step of adding an aqueous  
5 medium (water or a liquid medium containing water as a principal component) in a mixture made of a binder resin, a colorant, and an organic solvent, by gradually adding water to an organic continuous phase of the mixture, a water-in-oil discontinuous phase is formed, which is then converted into an  
10 oil-in-water discontinuous phase by further adding water, thus forming a suspension wherein the mixture in the form of particles (droplets) is suspended in the aqueous medium. At this time, those having a function for smoothly accelerating phase inversion of converting into an oil-in-water  
15 discontinuous phase from a water-in-oil discontinuous phase are referred to as a phase inversion accelerator.

[0075]

The binder resin employed in the present invention can be dispersed in the aqueous medium without employing the phase  
20 inversion accelerator because the binder resin is provided with the self-water dispersibility by neutralization. However, a powdered toner having a preferable average particle diameter and particle size distribution can be easily produced by employing the phase inversion agent in the binder resin  
25 used in the present invention.

[0076]

The following can be employed as the phase inversion accelerator in the present invention.

(i) Alcohol solvent

5 (ii) Metal salt compound

[0077]

As the alcohol solvent, for example, methanol, ethanol, isopropanol, n-propanol, isobutanol, n-butanol, t-butanol, sec-butanol, ethylene glycol monomethyl ether, propylene  
10 glycol monomethyl ether, ethylene glycol monomethyl ether or the like can be employed. As a matter of course, other alcohol solvents can also be employed. Preferred are isopropanol and n-propanol, which dissolve in water and have low boiling point. The amount of the alcohol solvent is  
15 within a range of about 10-50 parts by weight based on 100 parts by weight of the solid content of the resin, but is not limited thereto.

[0078]

As the metal salt compound, conventionally known metal  
20 salt compounds can be employed and preferred are those with metals having two or more valences and which dissolve in water. Examples thereof include barium chloride, calcium chloride, cuprous chloride, cupric chloride, ferrous chloride, and ferric chloride. The amount of the metal salt compound is  
25 within a range of about 0.01-3 parts by weight based on 100

parts by weight of the solid content of the resin, but is not limited thereto.

[0079]

The method of emulsifying/dispersing the mixture of the  
5 binder resin, the colorant, the organic solvent, the basic  
neutralizer and the phase inversion accelerator in the aqueous  
medium is not limited to a special method.

[0080]

In the method of the present invention, high shear  
10 emulsification/dispersion apparatuses and continuous  
emulsification/dispersion apparatuses can be employed, such as  
a Homomixer (produced by Tokushu Kika Kogyo Co., Ltd.), a  
Slasher (produced by Mitsui Mining Co., Ltd.), a Cavitron  
(produced by Eurotec, Ltd.), a Microfluidizer (produced by  
15 Mizuho Kogyo Co., Ltd.), a Munton-Golin Homogenizer (produced  
by Golin Co.), a Nanomizer (produced by Nanomizer Co., Ltd.),  
a Static Mixer (produced by Noritake Company) and the like.

[0081]

However, preferred is a method of adding dropwise water  
20 while stirring at low shear employing a stirrer, an anchor  
blade, a turbine blade, a faudler blade, a full-zone blade, a  
max blend blade, a semicircular blade or the like at a  
circumferential speed within a range of 0.2-5 m/second, and  
preferably within a range of 0.5-4 m/second, as disclosed in  
25 Japanese Unexamined Patent Application, First Publication No.

Hei 9-114135. By performing phase inversion at such low shear, formation of fine powders can be inhibited and a toner with a more preferred uniform particle size distribution can be obtained.

5 [0082]

With respect to the suspension of the spherical or generally spherical colored resin particles obtained by the phase inversion, it is preferred that the organic solvent be removed by distillation means. Then, solid-liquid separation  
10 of the suspension of the colored resin particles is performed by means such as filtration and the particles are dried, thus making it possible to obtain toner particles.

[0083]

With respect to the suspension of the spherical or  
15 generally spherical colored resin particles obtained by the phase inversion, it is preferred that the organic solvent be removed and that the hydrophilicity of the particles themselves be further lowered by a reverse neutralization treatment wherein acidic and hydrophilic groups neutralized  
20 with an acid such as hydrochloric acid, sulfuric acid, phosphoric acid, acetic acid or oxalic acid on the surface of the particles are returned to an original functional group , followed by removal of water and further filtration and drying.

25 [0084]

The drying can be conducted by employing any of conventionally known methods, and may be conducted at a temperature where the toner particles are not thermally fused or agglomerated under normal pressure or reduced pressure.

- 5 The freeze-drying method can be employed. There is also a method of simultaneously separating and drying the toner particles from the aqueous medium employing a spray drier. The method of stirring and drying the powder under reduced pressure while heating at the temperature where the toner particles are not thermally fused or agglomerated and the method of employing a flush-jet dryer (produced by Seisin Kigyo Co., Ltd.) capable of drying instantly employing a heat-dry air flow are efficient and preferable.

[0085]

- 15 In the case in which the classification for removing coarse particles and microparticles to adjust the particle size distribution of the formed toner particles is required, it can be conducted by a conventionally known method employing an air-flow type classifying machine after completion of drying. In the state where the colored resin particles are dispersed in the aqueous medium, a method of classifying by a centrifugal separator may be employed. The removal of the coarse particles can also be conducted by filtering water slurry of the toner particles employing a filter or a wet vibration sieve. With respect to the particle size
- 20
- 25



distribution of the toner, a ratio of 50% particle volume diameter ( $D_v$ ) to 50% number particle diameter ( $D_n$ ) as measured by a Coulter Multisizer is preferably 1.35 or less, and preferably 1.25 or less, because good image is easily  
5 obtained.

[0086]

The volume-average particle diameter of the color toner for electrostatic image development of the present invention is preferably within a range of 1-15  $\mu\text{m}$  in view of the  
10 resulting image quality, and is more preferably within a range of about 3-10  $\mu\text{m}$ . It is particularly preferably within a range of about 3-7  $\mu\text{m}$ . When the volume-average particle diameter is smaller, not only are improved the definition and gradation, but also the thickness of the toner layer for  
15 forming the printed image becomes smaller, thereby exerting the effect of reducing the amount of the toner to be consumed per page, which is preferable.

[0087]

In the present invention, various additives (referred to  
20 as external additives) can be employed to improve the surface of the toner base material, such as, for example, to increase the fluidity of the toner, to improve the charge characteristics thereof, or the like. Possible materials employed include, for example, inorganic microparticles such  
25 as silicon dioxide, titanium oxide, aluminum oxide, cerium

oxide, zinc oxide, tin oxide, zirconium oxide; products  
resulting when these are subjected to surface treatment  
employing a hydrophobic treating agent such as silicone oil or  
silane coupling agent; and fine particles made of resins such  
5 as polystyrene, acrylic, styrene-acrylic, polyester,  
polyolefin, cellulose, polyurethane, benzoguanamine, melamine,  
nylon, silicone, phenol, and vinylidene fluoride.

[0088]

Among these, silicon dioxide (silica), the surface of  
10 which has been subjected to hydrophobic treatment by means of  
various polyorganosiloxanes or silane coupling agents, is  
particularly advantageously employed. Such a product is  
commercially available under, for example, the following trade  
names.

15 [0089]

AEROSIL R972, R974, R202, R805, R812, RX200, RY200, R809,  
RX50, RA200HS, RA200H (Nippon Aerosil)

WACKER HDK H2000, H1018, H2050EP, HDK H3050EP, HVK2150  
(Wacker Chemicals East Asia)

20 NIPSIL SS-10, SS-15, SS-20, SS-50, SS-60, SS-100, SS-50B,  
SS-50F, SS-10F, SS-40, SS-70, SS-72F (Nippon Silica  
Industries)

CABOSIL TG820F, TS-530, TS-720 (Cabot Speciality  
Chemicals Inc.)

25 The particle diameter of the external additives is

preferably one-third or less that of the diameter of the colored particles, and more preferably one-tenth that diameter or less. Furthermore, these external additives may be simultaneously employed in two types having different average particle diameters.

[0090]

In the toner for non-magnetic one-component development, by using a toner having a large particle size in combination with a toner having a small particle size, the toner fluidity and development durability are improved, thereby preventing deposition on the blade of the developing machine and fogging and attaining long-term stability of charge during running, which is preferable.

[0091]

The amount of the external additive is within a range from 0.05-5% by weight, and preferably from 0.1-3% by weight, based on 100 parts by weight of the toner as the matrix.

[0092]

The silica can be externally added to the toner particles, employing a conventional powder mixer such as Henschel mixer and a so-called surface modifying machine such as hybridizer. This external addition treatment may be conducted so that the silica is deposited on the surface of the toner particles or a portion of the silica may be embedded into the toner particles.

[0093]

The toner of the present invention can be employed for development of an electrostatic latent image by means of the electrophotographic method, or employed as a one component  
5 developing agent, non-magnetic one component developing agent or a two component developing agent mixed with a carrier. The type of carrier is not specifically limited, and conventionally known carriers can be used such as iron powder, ferrite or magnetite, or carriers prepared by coating them  
10 with a resin.

[0094]

The toner of the present invention can be preferably employed in a printer of a so-called toner-jet system employing the method of directly spraying a powdered toner,  
15 which is charged frictionally by employing a non-magnetic one component developing apparatus having a developing agent bearing roller and a layer control member, over a paper on a back surface electrode through a hole on a flexible printed board with an electrode having a function of controlling the  
20 amount of the toner to be passed in the vicinity, thereby forming an image. Since the toner of the present invention is superior in fixation properties and color characteristics and has a spherical shape, it becomes easy to control scattering of the toner in a toner-jet system as compared with a toner  
25 having a nonuniform shape.

[0095]

[Examples]The following Examples further illustrate the present invention in detail, but the present invention is not limited thereto. In the following Examples and Comparative  
5 Examples, parts are by weight and water means deionized water, unless otherwise specified.

[0096]

(Synthesis Example of polyester resin)

Employing terephthalic acid (TPA) and isophthalic acid  
10 (IPA) as the dihydric carboxylic acid, polyoxypropylene(2.4)-2,2-bis(4-hydroxyphenyl)propane (BPA-PO) and polyoxyethylene(2.4)-2,2-bis(4-hydroxyphenyl)propane (BPA-EO) as the aromatic diol, and ethylene glycol (EG) as the aliphatic diol in each molar amount shown in Table 1,  
15 tetrabutyl titanate as the polymerization catalyst was charged in a separable flask in the amount of 0.3% by weight based on the total amount of monomers. The flask was equipped with a thermometer, a stirrer, a condenser and a nitrogen introducing tube at the upper portion and the mixture was reacted in a  
20 electrically heated mantle heater at 220°C for 15 hours in a nitrogen gas flow under normal pressure and, after gradually evacuating, the reaction was continued under 10 mmHg. The reaction was followed employing the softening point in accordance with the ASTM•E28-517 standard, and the reaction  
25 was completed by terminating evacuation when the softening

point reached a predetermined temperature to obtain a straight-chain polyester resin R1.

In the same manner as in R1, a resin R2 was synthesized. The composition and physical properties (properties) of the synthesized resins are shown in Table 1.

[0097]

[Table 1]

Table 1: Composition and properties of resin

Resin No.		R1	R2
Composition of resin	TPA	36.9	46.1
	IPA	9.2	
	BPA-PO	22.5	
	BPA-EO	11.3	33.8
	EG	20.1	20.1
		100 mol/%	100 mol/%
Properties of resin	Tl/2 temperature	100	96
	Acid value (KOH mg/g)	6.7	6.5
	Tg (°C)	54	55
	Mw (THF-soluble fraction)	5700	5600
	Mn (THF-soluble fraction)	2100	2600

10 [0098]

In Table 1, "Tl/2 temperature" is a value as measured by employing a Flow Tester "CFT-500" manufactured by Shimadzu Corporation as a constant load extrusion type capillary rheometer under the conditions of a nozzle diameter of 1.0 mmΦ × 1.0 mm, a load of 10 kg (cylinder pressure of 0.98 MPa) per unit area (cm<sup>2</sup>) and a heating rate of 6°C/min. "Tg" as the glass transition temperature is a value as measured by measuring at a heating rate of 10°C per minute by the second run method employing a Differential Scanning Calorimeter "DSC-

50" manufactured by Shimadzu Corporation.

[0099]

(Preparation Example of releasant and releasant dispersion)

- 5        105 Parts of a releasant, 45 parts of a polyester resin (R1 in Table 1) and 280 parts of methyl ethyl ketone were charged in a ball mill and, after stirring for 18 hours, the mixture was taken out and the solid content was adjusted to 20% by weight to obtain releasant microdispersions (W1-W3).
- 10    The produced releasant dispersions are shown in Table 2.

[0100]

[Table 2]

Table 2: Releasant dispersions

Releasant dispersion	W1	W2	W3
Releasant	Synthetic ester	Carnauba wax	PP
Polyester resin	R1	R1	R1
Weight ratio of Releasant/resin	70/30	70/30	70/30
Solid content (% by weight)	20	20	20

- 15    [0101]

Releasants shown in Table 2 are as follows.

Synthetic ester: tetrabeheenate ester of pentaerythritol

Carnauba wax: purified carnauba wax No. 1 (manufactured by CERA RICA NODA Limited, acid number: 5)

- 20    PP: "Viscol 660P" (polypropylene wax produced by Sanyo Chemicals).

[0102]

(Preparation Example of colorant dispersion)

A colorant, a resin and methyl ethyl ketone were charged in a ball mill so that the solid content becomes 35-50% and, after stirring for 18 hours, the mixture was taken out and the solid content was adjusted to 20% by weight to obtain colorant dispersions (P1-P4). Properties of the resulting colorant dispersions are shown in Table 3.

[0103]

[Table 3]

10 Table 3: Colorant dispersions

Releasant dispersion	P1	P2	P3
Colorant	Pigment of Formula 1	C.I. PIGMENT RED 57:1	C.I. PIGMENT RED 122
Resin	R1	R1	R1
Weight ratio of releasant/resin	50/50	50/50	50/50
Solid content on dispersion (%)	40	40	40
Dispersion time (Hour)	18	18	18
Final solid content (%)	20	20	20

[0104]

Colorants shown in Table 3 are as follows.

[0105]

15 C.I.PIGMENT RED 57:1; Symuler Brilliant Carmin 6B 285

(manufactured by Dainippon Ink and Chemicals, Inc.)

C.I.PIGMENT RED 122; Fastogen Super Magenta R (manufactured by



Dainippon Ink and Chemicals, Inc.)

(Preparation of wet kneaded mill base)

The above colorant dispersion, a resin and methyl ethyl ketone were mixed employing a despa and the solid content was  
5 adjusted to 50% to obtain mill bases (MB1-MB7). Each  
formulation of the mill bases thus prepared is shown in Table  
4.

[0106]

[Table 4]

10 Table 4: Formulation of mill bases

Mill base	Colorant dispersion	Polyester resin	MEK	Solid content
MB1	P1 = 100 parts	R1 = 80 parts	20 parts	50%
MB2	P1 = 200 parts	R1 = 60 parts	-	38%
MB3	P1 = 100 parts	R2 = 80 parts	20 parts	50%
MB4	P2 = 100 parts	R1 = 80 parts	20 parts	50%
MB5	P3 = 100 parts	R1 = 80 parts	20 parts	50%

[0107]

(Example 1)

600 parts of MB1 shown in Table 4, 100 parts of W1 shown  
15 in Table 2, 57.5 parts of methyl ethyl ketone, 29.0 parts of  
isopropyl alcohol as the phase inversion accelerator and 25.8  
parts of an aqueous 1 N ammonia solution were charged in a  
cylindrical vessel, followed by sufficient stirring.  
Subsequently, 230 parts of water was added and the liquid  
20 temperature was raised to 30°C. Then, 44 parts of water was  
added dropwise while stirring, thereby performing phase  
inversion emulsification. The circumferential speed was 1.05

m/second. After the stirring was continued for 30 minutes, the rotation was terminated and 400 parts of water was added.  
[0108]

Water slurry of particles was observed by an optical  
5 microscope. As a result, agglomerates of the releasant were not observed and a flowing releasant was not observed. The particle size distribution was measured by a Coulter Counter. As a result,  $D_v/D_n$  was 1.31 and the occurrence of coarse particles was not observed.

10 [0109]

The solvent was removed by vacuum distillation, followed by filtration and washing with water. The resulting wet cake was dispersed again in water and, after controlling the pH of the dispersion to 4 by adding an aqueous 1 N hydrochloric acid  
15 solution, filtration and washing with water were repeated. The wet cake thus obtained was freeze-dried and then classified by an air-flow type classifying machine to obtain toner particles having the volume-average particle diameter of 6.5  $\mu\text{m}$  and the average roundness of 0.981.

20 [0110]

The resulting toner particles were embedded into a resin and the resulting sample was cut by a microtome, and then the cross section dyed with ruthenium tetroxide was observed by TEM (transmission electron microscope). As a result, it was  
25 observed that the pigment and wax were included in the binder

resin and dispersed in particles nearly uniformly. Employing a Henschel mixer, 2 parts of a hydrophobic silica (SILICA RY200, manufactured by (Nippon Aerosil) was externally added to 100 parts of the resulting toner particles to obtain a powdered toner (toner for electrostatic image development).

[0111]

(Example 2)

790 Parts of MB2 shown in Table 4, 100 parts of W2 shown in Table 2, 28.0 parts of isopropyl alcohol as the phase inversion accelerator and 26.5 parts of an aqueous 1 N ammonia solution were charged in a cylindrical vessel, followed by sufficient stirring. Subsequently, 230 parts of water was added and the temperature was raised to 30°C. Then, 44 parts of water was added dropwise while stirring, thereby performing phase inversion emulsification. The circumferential speed was 1.05 m/second. After the stirring was continued for 30 minutes, the rotation was terminated and 400 parts of water was added.

[0112]

Water slurry of particles was observed by an optical microscope. As a result, agglomerates of the releasant were not observed and a flowing releasant was not observed. The particle size distribution was measured by a Coulter Counter. As a result,  $D_v/D_n$  was 1.34 and the occurrence of coarse particles was not observed.

[0113]

The solvent was removed by vacuum distillation, followed by filtration and washing with water. The resulting wet cake was dispersed again in water and, after controlling the pH of the dispersion to 4 by adding an aqueous 1 N hydrochloric acid solution, filtration and washing with water were repeated. The wet cake thus obtained was freeze-dried and then classified by an air-flow type classifying machine to obtain toner particles having the volume-average particle diameter of 5.1  $\mu\text{m}$  and the average roundness of 0.982.

[0114]

The resulting toner particles were embedded into a resin and the resulting sample was cut by a microtome, and then the cross section dyed with ruthenium tetroxide was observed by TEM (transmission electron microscope). As a result, it was observed that the pigment and wax were included in the binder resin and dispersed in particles nearly uniformly. Employing a Henschel mixer, 2 parts of a hydrophobic silica (SILICA RY200, manufactured by (Nippon Aerosil) was externally added to 100 parts of the resulting toner particles to obtain a powdered toner (toner for electrostatic image development).

(Comparative Example 1)

85 Parts of the resin R1 shown in Table 1, 5 parts of a tetrabehenate ester of pentarythritol as the releasant and 10 parts of a pigment of formula 1 as the colorant were kneaded

in a twin-screw extruder and the kneaded mixture was pulverized and then classified to obtain a powdered toner (Comparative Example 1-1) having the volume-average particle diameter of 5.4  $\mu\text{m}$  and a powdered toner (Comparative Example 1-2) having the volume-average particle diameter of 7.6  $\mu\text{m}$ , respectively. The resulting powdered toners were observed by TEM (transmission electron microscope) in the same manner as in the case of those of Examples 1 and 2. As a result, the pigment and wax was partially exposed on the surface of any of the toner particles.

[0115]

(Other Examples and Comparative Examples)

The powdered toners of the other Examples and Comparative Examples were produced in the same manner as in Example 1.

The powdered toner of Example 5 was produced in the same manner as in Example 2. The amount of MB (mill base) and the releasant dispersion, and measured value of average roundness of the powdered toners of the respective Examples and Comparative Examples are shown in Table 5.

[0116]

[Table 5]

Table 5

	Mill base	Releasant dispersion	Dv ( $\mu\text{m}$ )	Average roundness	Particle size distribution
Example 1	MB1 600 parts	W1 100 parts	6.5	0.981	1.31
Example 2	MB2 790 parts	W2 100 parts	5.1	0.982	1.34
Comp. Example 1-1		Synthetic ester	5.4	0.920	
Comp. Example 1-2		Synthetic ester	7.6	0.898	
Example 3	MB3 600 parts	W1 100 parts	7.2	0.976	1.37
Example 4	MB1 600 parts	W3 100 parts	5.4	0.978	1.43
Example 5	MB2 790 parts	W1 100 parts	6.9	0.980	1.43
Comp. Example 2	MB4 600 parts	W1 100 parts	5.6	0.976	1.31
Comp. Example 3	MB5 600 parts	W1 100 parts	5.7	0.976	1.33

Notation in Table 5

Synthetic ester: tetrabehenate ester of pentarythritol

[0117]

(Fixation properties test)

With respect to the fixation temperature range, the fixation temperature was determined by the following fixation properties test and the range between the upper limit and the lower limit was taken as the fixation temperature range. Employing each of the powdered toners of the Examples and Comparative Examples, the respective test samples were made by forming an unfixed image on a paper by a transformed printer that employs a commercially available organic semiconductor as a photosensitive material, and then fixed by passing through a heat roller (oilless type) Richo Imadio DA-250 at a speed of 90 mm/second, and then a Cellophane tape was applied on the image after fixation. The surface temperature range of the heat roller when ID (image density) after peeling is 90% or more of the original ID and offset does not occur was defined as a "fixation temperature". The results are shown in Table 6.

[0118]

(Printing Test)

Employing a commercially available negatively charging type non-magnetic single-component development system printer, the fogging, definition, gradation, OHP permeability, transfer efficiency and image density of the powdered toners of the respective Examples and Comparative Examples were evaluated.

The evaluation results are shown in Table 6. With respect to the fogging, definition and gradation, the images were visually observed employing a test pattern. The results were evaluated by the following criteria.

5       ○: better than standard

      ◎: even better

The transfer efficiency was shown by the values determined by the following method of measuring the transfer efficiency.

(Method of measuring the transfer efficiency)

10       Employing a commercially available negatively charging type non-magnetic one-component development system printer, a solid image (100 mm long and 20 mm broad) was developed and the printer was stopped when the solid image on the photosensitive material passed through the transferring portion by 50%.

15       Then, the image on the photosensitive material after transferring the non-transferred image (solid) was completely peeled off by a tape (30 mm × 20 mm) and the amount of the toner of the non-transferred image and the amount of the toner after transferring were measured. The transfer efficiency (%)

20       is calculated by the following equation.

$$\text{Transfer efficiency} = 100 - \frac{\text{amount of toner after transferring}}{\text{amount of toner of non-transferred image}} \times 100$$

[0119]

Furthermore, the OHP transparency was evaluated by the following method of evaluating the OHP sharpness.



## (Method of evaluating OHP sharpness)

A non-fixed image due to a color toner was formed on an OHP sheet and the non-fixed image was fixed by a separately prepared fixing tester. The OHP sheet was fixed by passing  
5 through a heat roller (oilless type) Richo Imadio DA-250 at a heat roller temperature of 160°C at a speed of 90 mm/second. A black-printed OHP sheet was placed on the OHP sheet made in the above procedure and was projected on a screen by an overhead projector, and then the sharpness of letters was  
10 visually observed. The results were evaluated by the following criteria.

○: sharp letters

×: blurred letters

[0120]

15 [Table 6]

Table 6

	Fogging	Definition	Gradation	OHP permeability	Transfer efficiency (%)	Fixation temperature range (°C)
Example 1	○	○	○	○	97	115-150
Example 2	⊙	⊙	⊙	⊙	98	115-150
Comp. Example 1-1	×	×	×	×	84	120-150
Comp. Example 1-2	standard	standard	Standard	standard	85	120-150
Example 3	⊙	○	○	○	97	115-150
Example 4	○	⊙	○	Standard	98	125-155
Example 5	⊙	⊙	○	⊙	98	115-150
Comp. Example 2	standard	○	Standard	standard	92	115-150
Comp. Example 3	standard	○	Standard	standard	91	120-150

[0121]

It was confirmed from the results shown in Table 6 that the toners of the Examples of the present invention are superior in fogging, definition, gradation and transfer efficiency. OHP permeability was also evaluated. It was confirmed that clear projected images having an excellent transparency can be obtained in all Examples. Using the toners of the respective Examples, a coated paper having a matte surface was printed. As a result, printed images having a sufficient density were obtained in a small coating weight. Moreover, the resulting prints had a subdued tone without unnecessary gloss at the solid portion and without deteriorating a matte surface condition of a paper.

[0122]

15 (Example 8)

As for the toner of Example 2, silicoon coat ferrite carrier (particle diameter of 80  $\mu\text{m}$ ) and toner density were mixed so as to be 3% by weight, and an image was produced with a two-component development system printer and tested. As a result, a printed image superior in fogging, definition, gradation and OHP permeability was obtained. Transfer efficiency was also superior.

(Comparative Example 4)

Using the toner of Comparative Example 1-2, a printing test was performed in the same manner as for Example 8, but

the fogging, definition, gradation, OHP permeability and transfer efficiency were each inferior to the toner used in Example 8.

(Comparative Example 5)

5        Using the toner of Comparative Example 3, a printing test was performed in the same manner as for Example 8, but the fogging, definition, gradation, OHP permeability and transfer efficiency were each inferior to the toner used in Example 8.

[0123]

10    [Effects of the Invention]

As explained above, the color toner for electrostatic image development of the present invention uses an organic pigment having a specific structure and by making the particle round and with a reduced diameter is made superior in transfer  
15 efficiency, definition and gradation.

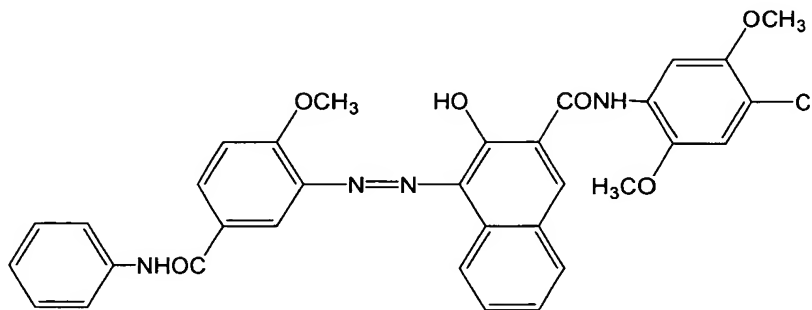
[Document Type] Abstract

[Abstract]

[Problem to be Solved by the Invention] To provide a color toner for electrostatic image development, which gives a clear printed image and also which gives an image having a transparency fixed on an OHP sheet and can achieve a clear color free from turbidity when projected on a screen. Another object of the present invention is to provide a color toner for electrostatic image development having a small particle size, which has a large content of a colorant as compared with a conventional color toner and which is transferred onto a material to be printed, such as paper, at a high transfer efficiency.

[Means for Solving the Problem] A color toner for electrostatic image development containing at least a binder resin and an organic pigment of the following formula 1, wherein an average roundness of the color toner defined in the following equation 1 is 0.97 or more.

Formula 1:



Equation 1:

$$\text{Average roundness} = \frac{\text{Perimeter of a circle having the same area as that of a projected area of particles}}{\text{Perimeter of a projected image of particles}}$$

[Elected Drawing]